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entitled (54) NITROPYRIMIDINE DERIVATIVES

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Related Art (56)	43847/68	87.16
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		09.53
	81055/75	87.17, 09.62-420

The following statement is a full description of this invention, including the best method of performing it known to us :

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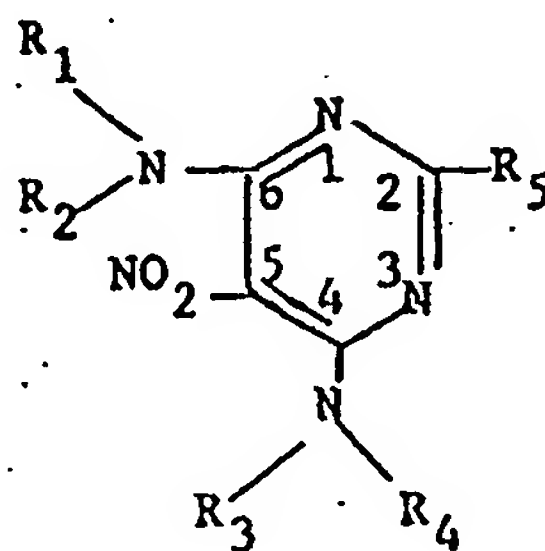
The present invention relates to agents which inhibit plant growth, in particular herbicidal agents which contain pyrimidine derivatives as active substances, as well as to new 5-nitropyrimidine derivatives with herbicidal properties. The invention relates also to a process for combating weeds which comprises the use of such active substances and of agents which contain them.

Specific 2,4-bis(substituted amino)-pyrimidines are described in French patent 1,572,620 as fungicides and insecticides. Dutch Auslegeschrift 68,14057 cites substituted pyrimidines which have a fungicidal action chiefly on phytopathogenic fungi on fruit and vegetable plants.

Finally, herbicidal and plant growth regulating 2-alkylthio-5-nitro-4,6-bis-amino-pyrimidines are described in French patent No. 2'137'933.

The surprising discovery has now been made that the 5-nitropyrimidines of the formula I, as well as their addition salts, are able to exert an inhibiting effect on the plant metabolism without causing significant damage to emergent plants as a postemergent herbicide and are better in some respects than the active ingredients of French patent 2'137'933.

The active substances of the agents according to the invention have the formula I



(I).

wherein R_1 represents an alkyl radical with 1 to 6 carbon atoms, an alkenyl radical with at most 5 carbon atoms, a C_3-C_6 cycloalkyl (unsubstituted or carrying methyl or ethyl substituents), lower alkoxyalkyl, hydroxyalkyl or cyanoalkyl radical, R_2 and R_3 each independently represents hydrogen or an alkyl radical with 1 to 4 carbon atoms, R_4 represents a C_3-C_6 alkenyl or C_3-C_6 cycloalkyl (unsubstituted or carrying methyl or ethyl substituents) radical, and R_5 represents hydrogen or a lower alkoxy, alkyl, haloalkyl, alkylamino or dialkylamino radical or represents a halogen atom.

In formula I, lower alkyl radicals are straight-chain or branched radicals with 1 to 6 carbon atoms, e.g. methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec.butyl, tert. butyl, n-pentyl, n-hexyl, and the isomers of the alkyl radicals with 5 and 6 carbon atoms. The lower straight-chain or branched alkyl radicals also form the alkyl moiety of alkoxy, haloalkyl, hydroxalkyl, cyanoalkyl, and alkylamino substituents.

In formula I, alkenyl radicals are straight-chain or branched radicals with 3 to 5 carbon atoms, e.g. propenyl, butenyl, pentenyl radicals; preferred radicals are allyl, methallyl, 3-methyl-butenyl or n-butenyl. As examples of cycloalkyl radicals with 3 to 6 ring carbon atoms there may be mentioned cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl. These rings can be substituted by methyl or ethyl.

The preferred haloalkyl radical is trifluoromethyl and trichloromethyl. Halogen is to be understood as meaning fluorine, chlorine, bromine, and iodine.

By addition salts are meant the salts with inorganic and organic strong acids, preferably hydrochloric acid, hydro-

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bromic acid, phosphoric acid, sulphuric acid, nitric acid, fluoroboric acid (HBF_4), perchloric acid, methylsulphuric or ethylsulphuric acid, halobenzoic acids, trichloroacetic acid, and aromatic sulphonic acids, such as methanesulphonic acid or p-toluenesulphonic acid.

Preferred compounds are those of the formula I and their salts, wherein R_1 represents an alkyl radical with 2 to 6 carbon atoms, a cycloalkyl radical with 3 to 5 carbon atoms, or an alkenyl radical with 3 or 4 carbon atoms, R_2 represents hydrogen, R_3 represents hydrogen or the methyl group, R_4 represents the methyl, ethyl or isopropyl group, and R_5 represents the methoxy radical, the methyl or ethyl radical, the trifluoromethyl or trichloromethyl radical, but especially the methyl radical.

Particularly preferred active substances of the formula I are also those in which the substituted amino radicals in 4- and 6-position are not identical and/or at least one of the radicals R_1 and R_4 is a branched alkyl radical with 3 to 5 carbon atoms.

The active substances contained in the agents according to the invention influence the plant growth in varying manner. Thus first and foremost they inhibit, delay, and prevent germination. As already mentioned, the pyrimidine derivatives of the formula I are not phytotoxic towards the emergent plants when used in the conventional rates of application, but they inhibit the growth in height of individual plant species and also promote bud dormancy. With very high rates of application

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of over 10 kg of active substance per hectare, the plants can also be damaged in varying degrees and can even die. A number of active substance of the formula I also possess in addition fungicidal, in particular plant-fungicidal, action.

The new agents are particularly suitable for treating cereals and grass crops. In the case of cereals, the growth in height is diminished without any reduction of the crop yield. By treating, for example, emergent summer cereals, rye, oats, and rice (plants in the 2-leaf stage) with 0.5 % dispersions of the following active substances:

2-methyl-4-ethylamino-6-(3'-pentyl-amino)-5-nitropyrimidine,
2-methoxy-4,6-bis-ethylamino-5-nitropyrimidine,
2-methyl-4,6-bis(ethylamino)-5-nitropyrimidine,
2-methoxy-4-(3'-pentylamino)-5-nitro-6-ethylamino-pyrimidine,
2-methyl-4-(2'-pentylamino)-6-ethylamino-5-nitro-pyrimidine,
2-chloro-4,6-bis(isopropylamino)-5-nitro-pyrimidine

there is obtained after 21 days a 50 to 60 % inhibition of the growth in height. The plants are sturdy and dark green. Similar results are obtained by treating ornamental plants, e.g.

Impatiens spp., Chrysanthemum and soya with 0.1 % active substance dispersions. The condition of the test plants is also very good. By treating existing grass crops, the growth in length of the grasses is delayed and the tillering increased. Weeds occurring in meadow grass, e.g. the strongly and rapidly seeding *Poa annua*, dandelions, plantaginaceae, thistles etc., are very severely inhibited in their germination and emergence

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and to all intents and purposes eliminated from existing grass crops. The inhibition of the growth in height in a grass mixture consisting of *Poa pratensis*, *Festuca ovina*, *Festuca rubra* and *Lolium*, is between 30 and 70 % (rate of application 5 kg/ha).

Further, the active substances, or the corresponding agents, can also be used as growth regulators for decreasing the setting of fruit or for thinning out fruit clusters, for fruit abscission, e.g. of citrus fruit or for delaying blossoming, and also as defoliants and for preventing undesirable formation of side shoots (tobacco, tomatoes, ornamental plants, vines etc.). To be particularly highlighted is the use of the active substances for inhibiting the growth of side shoots in tobacco and suppressing shoots in dormant tubers, for example those of ornamental plants, in potatoes, or in onions. Nitropyrimidines of the formula I when applied in small rates of application impart to the treated plant an increased resistance to drought, frost, and increased salt content in the soil, and increase the sugar content of sugar cane.

First and foremost, however, the new agents can be used as preemergence herbicides in food crops of the most diverse kind, such as cereals, maize, rice, cotton, soya, sorghum, sugar beet, potatoes, beans, ground nuts etc. The rates of application vary and depend on the time of application. They are between 0.1 and 10 kg of active substance per hectare in preemergence application and preferably up to 5 kg per

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hectare for treating existing grass crops, Normally up to 30 kg of active substance is used to prevent the growth of weeds in e.g. railway embankments, factory premises, and roads etc.

Herbicidal action in preemergence application

a) The active substances are mixed with compost earth in concentrations of 32 mg of active substance per litre of earth (=16 kg/ha) and 8 mg of active substance per litre of earth (= 4 kg/ha). The following test plants are sowed in this earth (seed dishes 5 cm deep filled with earth):

Solanum lycopersianum

Setaria italica

Avena sativa

Lolium perenne

Sinapis alba

Stellaria media

The seed dishes are then kept at 22°C to 25°C and 50 to 70 % relative humidity. The test is evaluated after 20 days. The evaluation is according to the following rating:

1 = plants dead

2-8 = intermediate stages of damage

9 = plants undamaged (control)

b) Immediately after the test plants have been sowed, the active substances are applied as an aqueous suspension, obtained from a 25 % wettable powder, to the surface of the earth. The seed dishes are then kept at 22°C to 23°C and 50 to 70 % relative humidity. The test is evaluated after 28

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days. As test plants there are used:

Weeds:

Cyperus esculentus
Lolium multiflorum
Alopecurus myosuroides
Digitaria sanguinalis
Amaranthus docendens
Setaria italica
Echinochloa crus galli
Rottboellia exalt.

Crop plants:

soya (Glycine hyspida)
cotton (Gossypium herbaccara)
maize (Zea Mais)
wheat (Triticum vulgare)
lucerne (Medicago sativa)
rice (Oryza)
sugar beet
Sorghum hybridum

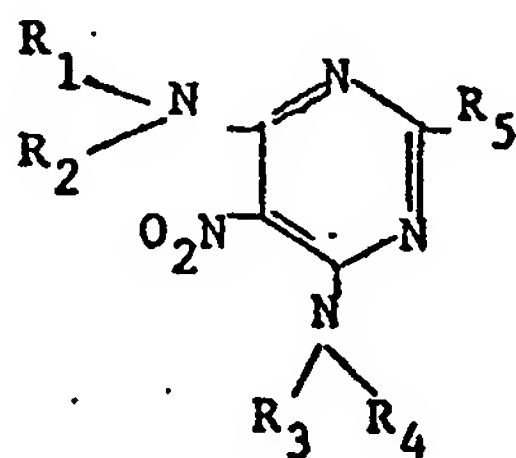
Evaluation is effected according to the rating given under a).
The rates of application are 2 and 4 kg of active substance/ha.
In these tests, the agents according to the invention exhibited
an excellent herbicidal action on the indicated test weeds.
Crop plants are not damaged.

In accordance with method b) various compounds of the
following list were tested. In the subsequent table, the
ratings obtained at rates of application of 4 kg/ha stand in

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front of the comma and those obtained at rates of application of 2 kg/ha stand after the comma.

Lists of active substances of the formula I



Compound	R ₁	R ₂	R ₄	R ₃	R ₅	Physical Data (°C)
1	CH ₃	H	CH ₃	H	C ₂ H ₅	m.p. 169-170°
2	i-C ₃ H ₇	H	i-C ₃ H ₇	H	C ₂ H ₅	m.p. 55-60°
3	C ₂ H ₅	H	C ₂ H ₅	H	C ₂ H ₅	m.p. 65-68°
4	-CH(C ₂ H ₅) ₂	H	C ₂ H ₅	H	C ₂ H ₅	n _D ²⁰ = 1,5635
5	C ₂ H ₅	H	CH ₃	CH ₃	C ₂ H ₅	n _D ²⁰ = 1,5893
6	CH ₂ =CH-CH- CH ₃	H	C ₂ H ₅	H	C ₂ H ₅	
7	-CH(CH ₃)-C ₂ H ₅	H	C ₂ H ₅	H	C ₂ H ₅	n _D ²⁰ = 1,5640
8	-CH(CH ₃) ₂	H	C ₂ H ₅	H	C ₂ H ₅	n _D ²⁰ = 1,5620
9	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	n _D ²⁰ = 1,5760
10	-C(CH ₃) ₃	H	C ₂ H ₅	H	C ₂ H ₅	n _D ²⁰ = 1,5615
11	CH ₃	H	C ₂ H ₅	H	i-C ₃ H ₇	m.p. 50-52°
12	i-C ₃ H ₇	H	i-C ₃ H ₇	H	i-C ₃ H ₇	m.p. 45°
13	C ₂ H ₅	H	C ₂ H ₅	H	i-C ₃ H ₇	m.p. 28°
14	-CH(CH ₃)-C ₃ H ₇	H	C ₂ H ₅	H	i-C ₃ H ₇	n _D ²⁰ = 1,5532
15	CH ₃	H	CH ₃	H	i-C ₃ H ₇	m.p. 101-102°
16	i-C ₃ H ₇	H	C ₂ H ₅	H	i-C ₃ H ₇	n _D ²⁰ = 1,5660
17	-CH(C ₂ H ₅) ₂	H	C ₂ H ₅	H	i-C ₃ H ₇	n _D ²⁰ = 1,555
18	-CH-CH ₂ -CH(CH ₃) ₂	H	C ₂ H ₅	H	i-C ₃ H ₇	n _D ²⁰ = 1,5558
19	C ₂ H ₅	H	CH ₃	CH ₃	i-C ₃ H ₇	m.p. 30-31°

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Compound	R ₁	R ₂	R ₄	R ₃	R ₅	Physical Data (°C)
20	-CH(CH ₃)C ₂ H ₅	H	C ₂ H ₅	H	CF ₃	n _D ²⁰ = 1,5209
21	C ₂ H ₅	H	C ₂ H ₅	H	CF ₃	m.p. 65-70°
22	i-C ₃ H ₇	H	i-C ₃ H ₇	H	CF ₃	m.p. 60-65°
23	-CH(C ₂ H ₅) ₂	H	C ₂ H ₅	H	CF ₃	n _D ²⁰ = 1,5175
24	CH ₃	H	CH ₃	H	CF ₃	m.p. 140-142°
25	-CH(CH ₃)C ₂ H ₅	H	C ₂ H ₅	H	CCl ₃	
26	i-C ₃ H ₇	H	i-C ₃ H ₇	H	CCl ₃	
27	-CH(CH ₃)C ₂ H ₅	H	i-C ₃ H ₇	H	CCl ₃	
28	Sec. C ₄ H ₉	H	CH ₃	H	-OCH ₃	m.p. 98-99°
29	i-C ₃ H ₇	H	i-C ₃ H ₇	H	-OCH ₃	m.p. 77-78°
30	tert. C ₄ H ₉	H	C ₂ H ₅	H	-OCH ₃	m.p. 59-60°
31	Sec. C ₄ H ₉	H	Sec. C ₄ H ₉	H	-OCH ₃	b.p. 157°/0,00 Torr
32	C ₂ H ₅	H	C ₂ H ₅	H	-OCH ₃	m.p. 103-105°
33	-CH(C ₂ H ₅) ₂	H	C ₂ H ₅	H	-OCH ₃	b.p. 162°/0,00 Torr
34	Sec. C ₄ H ₉	H	C ₂ H ₅	H	-OCH ₃	b.p. 138°/0,00 Torr
35	-CH(C ₂ H ₅) ₂	H	-CH(C ₂ H ₅) ₂	H	-OC ₂ H ₅	m.p. 45-47°
36	-CH(C ₂ H ₅) ₂	H	i-C ₃ H ₇	H	-OCH ₃	b.p. 145°/0,00 Torr
37	Sec. C ₄ H ₉	H	i-C ₃ H ₇	H	-OCH ₃	b.p. 160°/0,00 Torr
38	-CH(C ₂ H ₅) ₂	H	i-C ₃ H ₇	H	-OC ₂ H ₅	b.p. 150°/0,00 Torr
39	C ₂ H ₅	H	C ₂ H ₅	H	-OC ₄ H ₉	b.p. 185°/0,00 Torr
40	CH ₃	H	CH ₃	H	-OCH ₃	m.p. 167-168°
41	i-C ₃ H ₇	H	i-C ₃ H ₇	H	Cl	m.p. 128-130°
42	C ₂ H ₅	H	C ₂ H ₅	H	Cl	m.p. 130-132°
43	-CH(C ₂ H ₅) ₂	H	i-C ₃ H ₇	H	Cl	m.p. 58-60°
44	n-C ₆ H ₁₃	H	n-C ₆ H ₁₃	H	-NHC ₆ H ₁₃ (n)	m.p. 58-50°
45	i-C ₃ H ₇	H	i-C ₃ H ₇	H	-NH-i-C ₃ H ₇	b.p. 185°/0,00 Torr
46	C ₂ H ₅	H	C ₂ H ₅	H	-N(CH ₃) ₂	m.p. (crude) 102-105
47	-CH(C ₂ H ₅) ₂	H	i-C ₃ H ₇	H	-N(CH ₃) ₂	b.p. 160°/0,00 Torr

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Compound	R ₁	R ₂	R ₄	R ₃	R ₅	Physical Data (°C)
48	CH ₃	H	CH ₃	H	-NHCH ₃	m.p. 155-157°
49	Sec.C ₄ H ₉	H	Sec.C ₄ H ₉	H	H	b.p. 104°/0,00 Torr
50	C ₂ H ₅	H	C ₂ H ₅	H	H	m.p. 80-81°
51	-CH(C ₂ H ₅) ₂	H	CH ₃	CH ₃	H	b.p. 120°/0,00 Torr
52	-CH(C ₂ H ₅) ₂	H	i-C ₃ H ₇	H	H	
53	tert.C ₄ H ₉	H	tert.C ₄ H ₉	H	H	m.p. 106-107°
54	CH ₃	CH ₃	CH ₃	H	H	m.p. 96-97°
55	CH ₃	H	CH ₃	H	H	m.p. 192-193°
56	-CH(C ₂ H ₅) ₂	H	C ₂ H ₅	H	H	
57	-CH(CH ₃)C ₂ H ₅	H	C ₂ H ₅	H	H	
58	CH ₂ =CH-CH ₂ -	H	CH ₂ =CH-CH ₂ -	H	CH ₃	m.p. 70-72°
59	cyclopropyl	H	cyclopropyl	H	CH ₃	m.p. 147-148°
60	i-C ₃ H ₇	H	i-C ₃ H ₇	H	CH ₃	m.p. 99-101°
61	Sec.C ₄ H ₉	H	Sec.C ₄ H ₉	H	CH ₃	m.p. 36-39°
62	-CH(C ₂ H ₅) ₂	H	C ₂ H ₅	H	CH ₃	b.p. 140°/0,00 Torr
63	-CH(C ₂ H ₅) ₂	H	i-C ₃ H ₇	H	CH ₃	b.p. 100°/0,02 Torr
64	n-C ₆ H ₁₃	H	n-C ₆ H ₁₃	H	CH ₃	m.p. 41-43°
65	C ₂ H ₅	H	C ₂ H ₅	H	CH ₃	m.p. 109-111°
66	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	CH ₃	m.p. 58-60°
67	cyclopentyl	H	cyclopentyl	H	CH ₃	m.p. 71-73°
68	-C(CH ₃) ₂ CN	H	C ₂ H ₅	H	CH ₃	m.p. 76-78°
69	-CH ₂ -CH ₂ -OH	H	C ₂ H ₅	H	CH ₃	m.p. 128-130°
70	-CH ₂ -CH ₂ -OCH ₃	H	C ₂ H ₅	H	CH ₃	m.p. 64-66°
71	CH ₂ =CH-CH ₂ -	H	C ₂ H ₅	H	CH ₃	m.p. 77-79°
72	cyclopropyl	H	C ₂ H ₅	H	CH ₃	m.p. 118-119°
73	-CH(CH ₃)C ₂ H ₅	H	i-C ₃ H ₇	H	CH ₃	m.p. 40-42°
74	n-C ₄ H ₉	H	n-C ₄ H ₉	H	CH ₃	m.p. 60-62°
75	cyclohexyl	H	C ₂ H ₅	H	CH ₃	m.p. 78-80°
76	C ₂ H ₅	H	CH ₃	CH ₃	CH ₃	m.p. 98-99°

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Compound	R ₁	R ₂	R ₄	R ₃	R ₅	Physical Data (°C)
77	C ₄ H ₉	C ₄ H ₉	C ₄ H ₉	C ₄ H ₉	CH ₃	b.p. 180°/0 T _i
78	CH ₃	H	CH ₃	H	CH ₃	m.p. 200-20
79	-CH(CH ₃)-CH ₂ -OCH ₃	H	C ₂ H ₅	H	CH ₃	n ₂₀ ^D = 1,55
80	-CH(CH ₃)C ₃ H ₇	H	i-C ₃ H ₇	H	CH ₃	

The following Table I gives some results according to test method a):

Table I

Compound	Concentration kg/ha	Solanum	Setaria	Avena sat.	Lolium	Snaps	Stellaria
28	16	2	1	7	3	8	6
33	16	2	1	3	1	3	1
36	16	2	1	3	2	5	1
43	16	7	1	6	1	8	9
49	16	4	2	6	3	7	6
62	16 4		1	1 2		2 4	2

A number of results according to test method 1 are listed in the following Table 2: (ratings for 4 kg/h. before the comma, ratings for 2 kg/ha after the comma.

Table II

Weeds

Crop plants

Compound	Rottboellia exalt.	4,5 1,1 1,1 2,3 6,7 6,8 2,4 6,6 2,2 2,2
	Echinochloa crusgalli	2,3 1,1 1,1 1,1 1,2 2,2 1,2 2,3 1,1 1,1
	Setaria italica	2,6 1,1 1,1 1,2 7,7 4,7 4,5 2,8 1,1 1,1
	Amaranthus	3,4 1,1 2,2 3,4 2,2 5,9 3,4 3,4 1,1 1,2
	Digitaria sanguin.	1,3 1,1 1,1 2,2 1,3 2,3 1,1 2,2 1,1 1,1
	Alopecurus myos.	7,7 2,2 1,1 2,3 2,3 2,2 2,8 7,8 1,1 1,1
	Lolium multiflorum	8,8 2,3 1,2 3,3 3,5 3,3 2,6 7,8 1,2 1,2
	Cyperus esculentus	1 9 9 8 8 8 8 8 8 7
	Luzernes Medicago	9,9 8,9 9,9 9,9 9,9 8,9 7,8 7,9 5,6 6,8
	Wheat Triticum	8,8 7,9 9,9 5,7 9,9 9,9 7,8 3,8 5,6 2,3
	Maize Zea	6,6 9,9 3,7 8,8 9,9 9,9 8,9 8,9 7,8 3,6
	Sorghum hybridum	6,7 8,8 2,2 4,7 8,8 9,9 6,9 8,8 2,6 1,2
	Dry rice Oryza	6,8 2,7 3,8 6,6 6,7 4,5 2,6 6,6 3,3 7,7
	Water rice Oryza	1,1 1,2 3,4 3,4 3,4 3,4 3,4 3,4 3,4 3,4
	Goya Glycine	9,9 7,8 7,9 9,9 2,9 9,9 9,9 9,9 9,9 9,9
	Cotton	9,9 7,9 9,9 9,9 9,9 9,9 9,9 9,9 9,9 7,8
	Beta Sugar beet	6,7 4,9 6,7 9,9 9,9 8,9 8,9 7,9 2,2 3,7

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Agents containing the following active substances exhibited particularly good pre-emergent herbicidal properties:

2-chloro-4-isopropylamino-6-pentyl-(3)-amino-5-nitro-pyrimidine
2-chloro-4,6-bis-isopropylamino-5-nitro-pyrimidine
2-methoxy-4,6-bis-ethylamino-5-nitro-pyrimidine
2-methoxy-4-sec.butylamino-6-methylamino-5-nitro-pyrimidine
2-methoxy-4-ethylamino-6-tert.butylamino-5-nitro-pyrimidine
2-methoxy-4,6-bis-isopropylamino-5-nitro-pyrimidine
2-methoxy-4-sec.butylamino-6-ethylamino-5-nitro-pyrimidine
2-methoxy-4-pentyl-(3)-amino-6-ethylamino-5-nitro-pyrimidine
2-methyl-4-pentyl(3)-amino-6-ethylamino-5-nitro-pyrimidine
2-methoxy-4-isopropylamino-6-pentyl-(3)-amino-5-nitro-pyrimidine
2-dimethylamino-4-isopropylamino-6-pentyl-(3)-amino-5-nitro-pyrimidine
2-ethylamino-4-isopropylamino-6-pentyl-(3)-amino-5-nitro-pyrimidine

and the corresponding 2-isopropyl-pyrimidines and 2-trifluoro-methyl-pyrimidines.

Some active ingredients of formula I are highly suited for the post-emergent control of the problem weed *Avena fatua* in grain crops like wheat, barley and oats, and are in this respect superior to 2-methylthio-4-[pentyl-(3)amino]-6-isopropylamino-5-nitro-pyrimidine described in French patent 2'137'933 and even superior to "^(Registered Trade Mark)Suffix" [ethyl N-benzoyl N-(3',4'-dichlorophenyl)-2-amino propionate]. This is especially the case for 2-methyl-4-[pentyl-(3)amino]-6-ethylamino-5-nitro-pyrimidine of the present invention (compound No. 62 of the table; example 6).

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Herbicidal action towards Avena fatua in grain
crops in post-emergent application

Young wheat plants and Avena fatua are grown in a greenhouse in different pots of the dimensions 18.18.20 cm at temperatures of 15 to 17°C, until they reach the 2-leaves-state; then the plants are left to develop at day-temperatures of 15 to 20°C and night-temperatures of 5 to 7°C until they attain the 3- to 4-leaves-stage. At this stage, the pots with the plants are sprayed with aqueous suspensions of the active ingredients in 5 different concentrations. The evaluation of the results took place 66 days after the treatment. The temperature in the greenhouse during this period was 15 to 20°C.

Grain crop used: wheat (variety "hard"; variety "Probus";
variety "Zenith")

Weed used: Avena fatua (types France, Switzerland, Morocco)

Active ingredients:

- A = No. 62 of table (example 6 of this invention)
- B = 2-methylthio-4-[3'-pentylamino]-6-isopropylamino-
-5-nitro-pyrimidine (French patent 2'137'933)
- C = "Suffix" (known herbicide).

Concentration used:

8, 4, 2, 1 and 0,5 lb per acre (0,8; 0,4; 0,2; 0,1 and
0,05 g per m²)

Evaluation:

- 1 = plants completely destroyed
- 9 = plants undamaged (control)
- 2-8 = intermediate stages of damage.

Results

wheat varieties															Avena fatua, type														
"hard"					"Zenith"					"Probus"					France					Switzld.					Morocco				
8					4	2	1	0,5	8	4	2	1	0,5	8	4	2	1	0,5	8	4	2	1	0,5	8	4	2	1	0,5	
concentration (lb/acre):																													
<u>Compound:</u>																													
A (invention)					8	9	9	9	9	9	9	9	9	6	9	9	9	9	1	1	1	1	1	1	1	2	2	2	
B					4	4	6	8	9	8	8	9	9	9	4	6	7	9	9	1	2	2	4	4	1	3	5	5	
C					6	7	9	9	9	9	9	9	9	7	9	9	9	9	3	4	6	6	9	1	3	7	9	9	

Conclusions:

The compound A according to this invention shows, besides an equal or somewhat better tolerance towards different wheat varieties, a clearly better herbicidal action against different types of the weed Avena fatua, compared with the known products B and C, C being the well known "Suffix" of the market.

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The agents according to the invention are manufactured in known manner by intimately mixing and/or grinding active substances of the formula I with the suitable carriers, optionally with the addition of dispersants or solvents which are inert towards the active substances. The active substances may take and be used in the following forms:

Solid forms:

dusts, tracking agents, granules, coated granules, impregnated granules and homogeneous granules.

Liquid forms:

a) active substances which are dispersible in water;

wettable powders, pastes, emulsions;

b) solutions.

To manufacture solide forms (dusts, tracking agents), the active substances are mixed with solid carriers. Suitable carriers are, for example: kaolin, talcum, bolus, loess,

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chalk, limestone, ground limestone, attaclay, dolomite, diatomaceous earth, precipitated silica, alkaline earth silicates, sodium and potassium aluminium silicates (feldspar and mica), calcium and magnesium sulphates, magnesium oxide, ground synthetic materials, fertilisers, for example ammonium sulphate, ammonium phosphate, ammonium nitrate, urea, ground vegetable products, such as corn meal, bark dust, sawdust, nutshell meal, cellulose powder, residues of plant extractions, activated charcoal etc. These substances can either be used singly or in admixture with one another.

The particle size of the carriers for dusts is advantageously up to 0.1 mm, for tracking agents from about 0.075 to 0.2 mm, and for granules 0.2 mm or larger.

The solid forms contain the active substances in concentrations from 0.5% to 80%.

To these mixtures can also be added additives which stabilize the active substance and/or non-ionic, anionic and cationic surface active substances, which for example improve the adhesion of the active ingredients on plants or parts of plants (adhesives and agglutinants) and/or ensure a better wettability (wetting agents) and dispersibility (dispersing agents). Examples of suitable adhesives are the following: olein/chalk mixture, cellulose derivatives (methyl cellulose, carboxymethyl cellulose), hydroxyethyl glycol ethers of monoalkyl and dialkyl phenols having 5 to 15 ethylene oxide radicals per molecule and 8 to 9 carbon atoms in the alkyl radical, lignin sulphonic acids, their alkali metal and alkaline earth metal salts, polyethylene glycol ethers (carbowaxes), fatty alcohol polyethylene glycol ethers having 5 to 20 ethylene oxide radicals per molecule and 8 to 18 carbon atoms in the fatty alcohol moiety, condensation products of urea and formaldehyde, and also latex products.

The water-dispersible concentrates of the active substance i.e., wettable powders, pastes and emulsifiable concentrates, are agents which can be diluted with water to any concentration desired. They consist of active substance, carrier, optionally additives which stabilize the active substance, surface-active substances and anti-foam agents and, optionally, solvents. The active substance concentrations in these agents are from 5 - 80%.

Wettable powders and pastes are obtained by mixing and grinding the active substances with dispersing agents and pulverulent carriers in suitable apparatus until homogeneity is attained. Carriers are, for example, those mentioned for the solid forms of application. In some cases it is advantageous to use mixtures of different carriers. As dispersing agents there can be used, for example, condensation products of sulphonated naphthalene and sulphonated naphthalene derivatives with formaldehyde, condensation products of naphthalene or naphthalene sulphonic acids with phenol and formaldehyde, as well as alkali, ammonium and alkaline earth metal salts of lignin sulphonic acid, in addition, alkylaryl sulphonates, alkali and alkaline earth metal salts of dibutyl naphthalene sulphonic acid, fatty alcohol sulphates such as salts of sulphated hexadecanols, heptadecanols, octadecanols, and salts of sulphated fatty alcohol glycol ethers, the sodium salt of oleoyl, the sodium salt of olcoyl methyl tauride, ditertiary acetallene glycols, dialkyl dilauryl ammonium chloride and fatty acid alkali and alkaline earth metal salts.

Suitable anti-foam agents are silicones.

The active substance is so mixed, ground sieved and strained with the additives mentioned above that, in wettable powders, the solid particle size of 0.02 to 0.04 mm and in pastes, of 0.03 mm is not exceeded. To procure emulsifiable con-

centrates and pastes, dispersing agents such as those given in the previous paragraphs, organic solvents and water are used. Examples of suitable solvents are the following: alcohols, benzene, xylenes, toluene, dimethyl sulphoxide, and mineral oil fractions boiling between 120 and 350°C. The solvents must be practically odorless, not phytotoxic, inert to the active substances and not readily inflammable.

Furthermore, the agents according to the invention can be applied in the form of solutions. For this purpose the active substances or several active substances of general formula II are dissolved in suitable organic solvents, mixtures of solvents or in water. Aliphatic and aromatic hydrocarbons, chlorinated derivatives thereof, alkyl naphthalenes and mineral oils singly or in admixture, can be used as organic solvents. The solutions contain the active substance in a concentration range from 1 % to 20 %. These solutions can be applied either with a propellant gas (as spray) or with special sprays (as aerosol). The agents described according to the invention can be mixed with other biocidally active substances or agents. Thus in order to broaden the activity spectrum the new agents may contain, for example, insecticides, fungicides, bactericides, fungistatics, bacteriostatics or nematocides, in addition to the cited active substance of the formula I. The agents according to the invention may also contain plant fertilisers, trace elements etc.

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Granules

The following substances are used to produce 5% granules:

- 5 parts of active substance,
- 0.25 parts of epichlorohydrin,
- 0.25 parts of cetyl polyglycol ether,
- 3.50 parts of polyethyleneglycol,
- 91 parts of kaolin (particle size 0.3 - 0.8 mm).

The active substance is mixed with epichlorohydrin and dissolved with 6 parts of acetone; the polyethylene glycol and cetyl polyglycol ether are then added. The thus obtained solution is sprayed on kaolin, and the acetone subsequently evaporated in vacuo.

Wettable Powder

The following constituents are used to manufacture

a) a 50 %, b) a 25 % and c) a 10 % wettable powder:

- a) 50 parts of 2-methoxy-4-ethylamino-5-nitro-6-(pent-3'-ylamino)-pyrimidine
- 5 parts of sodium dibutyl-naphthalene sulphonate,
- 3 parts of naphthalenesulphonic acid/phenolsulphonic acid/formaldehyde condensate (3:2:1),
- 20 parts of kaolin,
- 22 parts of Champagne chalk;

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- b) 25 parts of 2-methyl-4-isopropylamino-5-nitro-6-methylamino-pyrimidine
- 5 parts of sodium oleylmethyltauride,
- 2.5 parts of naphthalenesulphonic acid/formaldehyde condensate,
- 0.5 part of carboxymethyl cellulose,
- 5 parts of neutral potassium aluminium silicate,
- 62 parts of kaolin;
- c) 10 parts of 2-dimethylamino-4-sec. butylamino-5-nitro-6-methylamino-pyrimidine,
- 3 parts of a mixture of the sodium salts of saturated fatty alcohol sulphates,
- 5 parts of naphthalenesulphonic acid/formaldehyde condensate.
- 82 parts of kaolin.

The indicated active substance is applied to the corresponding carriers (kaolin and chalk) and then these are mixed and ground, to yield wettable powders of excellent wettability and having an excellent capacity for forming suspensions. By diluting these wettable powders with water it is possible to obtain suspensions of every desired concentration of active substance. Such suspensions are used for combating weeds and grass-like weeds in food crops in the preemergence method and for treating grass crops.

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Paste

The following substances are used to manufacture a 45 % paste:

- 45 parts of 2-chloro-4-isopropylamino-5-nitro-6-(pent-3'-yl-amino)-pyrimidine,
- 5 parts of sodium aluminium silicate,
- 14 parts of cetyl polyglycol ether with 8 mols of ethylene oxide.
- 1 part of oleyl polyglycol ether with 5 mols of ethylene oxide,
- 2 parts of spindle oil,
- 10 parts of polyethylene glycol,
- 23 parts of water.

The active substance is intimately mixed with the addition in appropriate devices and ground. A paste is obtained from which, by diluting it with water, is possible to manufacture suspensions of every desired concentration of active substance. The suspensions are suitable for treating rose gardens.

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Emulsion Concentrate

To manufacture a 25 % emulsion concentrate

25 parts of 2-methyl-4-isopropylamino-5-nitro-6-pentyl(3)-amino-pyrimidine,

5 parts of a mixture of nonylphenolpolyoxy-ethoxy-ethylene and calcium, dodecylsulfonate,

35 parts of 3,5,5-trimethyl-2-cyclohexan-1-one,

35 parts of dimethyl formamide,

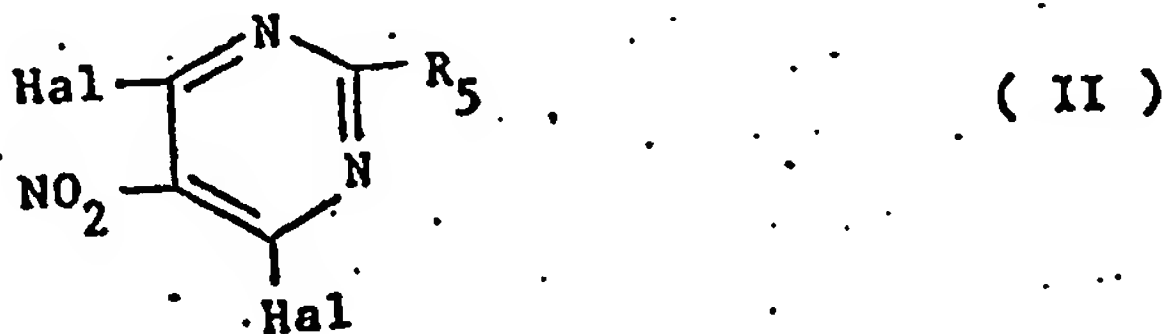
are mixed together. This concentrate can be diluted with water to give emulsions in desired concentrations. Such emulsions are suitable for combating weeds in food crops.

Instead of the respective ^{active} ~~active~~ substance used in the preceding formulations, it is also possible to use another of the compounds comprised by the formula I.

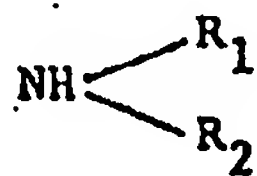
The new 5-nitropyrimidines of the formula I are

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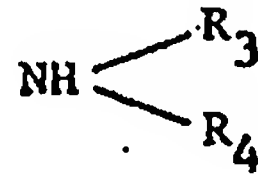
obtained according to the present invention by reacting a corresponding 4,6-dihalo-5-nitropyrimidine derivative of the formula II



wherein R_5 has the meanings indicated under formula I and Hal represents in each case a halogen atom, preferably chlorine or bromine, successively with amines of the formulae III and/or IV



(III)



(IV)

in the presence of an acid acceptor and optionally of a solvent and/or diluent. In the formulae II, III, and IV, the symbols R_1 to R_5 have the meanings indicated under the formula I.

The necessary stepwise exchange when using different amines of the formula III or IV is dependent both on temperature as well as on time and solvent. In general, the reaction temperatures are in the range from -60°C to $+120^{\circ}\text{C}$; for the exchange of the first halogen atom it is necessary to choose temperatures between -60°C to $+120^{\circ}\text{C}$ and for the exchange of the second halogen atom between 10°C and 50°C .

or higher.

Suitable solvents for the reactions according to the invention are water, ketones, such as acetone or methyl ethyl ketone, ethers and ethereal compounds, such as dioxan or tetrahydrofuran, aliphatic and aromatic hydrocarbons and halogenated hydrocarbons, also nitriles, such as acetonitrile, N,N-dialkylated amides, such as dimethyl formamide, or sulphoxides, such as dimethyl sulphoxide, as well as mixtures of such solvents.

The most suitable acid acceptors for the process according to the invention are inorganic bases, such as hydroxides, hydrogen carbonates and carbonates of alkali metals and alkaline earth metals. But tertiary amines, such as trialkylamines, dialkylamines, pyridine, and pyridine bases, are also possible as organic bases. It is also possible to use as acid acceptor the respective amino component of the formula III or IV in excess. Sodium hydroxide or potassium hydroxide are preferred.

After substitution of the radical of an amine of the formula III or IV for a halogen atom, it is possible to isolate 4(6)-amino-6-(4)-halo-5-nitropyrimidine derivatives as intermediates, some of which have not yet been described in the literature.

For the manufacture of 4,6-diamino-5-nitro-pyrimidine derivatives of the formula I, in which R_5 represents a dimethylamino group or the methoxy radical, there is used as starting material either 2,4,6-trihalo-5-nitropyrimidine or a 2-alkylthio-4,6-dichloro-5-nitro-pyrimidine derivative.

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The halogen atoms in 4- and 6-position are replaced in the manner described hereinbefore and the remaining halogen atom in 2-position is then replaced by the radical of the corresponding amine or alcohol.

The reaction temperature for this process step are from 30°C to 120°C. Suitable acid acceptors and suitable solvents or diluents are those cited hereinbefore.

The desired 4,6-diamino-5-nitro-2-alkoxy-pyrimidines are obtained by substituting the radical RO for the RS group of a 2-alkylthio-4,6-diamino-pyrimidine using an alkanolate, for example an alkali metal methylate, in the presence of a solvent or diluent, preferably of the alkanol corresponding to the alkanolate, or also of dimethyl sulphoxide, dimethyl cellosolve etc., at temperatures between 0°C and 130°C.

Addition salts are manufactured by reacting the pyrimidine derivatives of the formula I in known manner with inorganic and organic acids. The strong acids, e.g. hydrohalic acids, sulphuric acid, fluoroboric acid, phosphoric acid, alkylsulphuric acid, are preferred for the pyrimidine derivatives of the formula I.

The following Examples will serve to illustrate the process for the manufacture of the described compounds. These and other pyrimidine derivatives of the formula I manufactured by the methods described in the Examples have already been listed in the opening portion of the description.

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Example 1

a) 50 g of ethylamine gas are slowly passed into a solution of 60.0 g of 2-methylthio-4,6-dichloro-5-nitro-pyrimidine in 750 ml of absolute ethanol at about 35°C and without cooling. The mixture is subsequently stirred for 2 hours at room temperature and concentrated to dryness in vacuo at 45°C. The residue is suspended in 500 ml of water, isolated, and washed with water. The product is recrystallised from a mixture of hexane and pentane in the ratio 10:1. The 2-methylthio-4,6-bis-ethylamino-5-nitro-pyrimidine has a melting point of 130°-131°C.

b) 11.25 g of 4,6-diethylamino-2-methylthio-5-nitro-pyrimidine are added to 200 ml of absolute methanol. Then 20 ml of triethylamine and subsequently a solution of 3.2 g of sodium methylate in 50 ml of absolute methanol are added. This mixture is stirred for 20 hours at 90°C under reflux, then cooled to room temperature. The solution is then poured into 2 litres of ice water and the temperature is kept at 25°C with a little ice. The precipitated crystals are filtered off with suction, washed with water, and dried in a water jet vacuum at 70°C over KOH for 16 hours. Yield: 9.3 g of 2-methoxy-4,6-bis-ethylamino-5-nitro-pyrimidine with a melting point of 98°-100°C. Recrystallisation from isopropyl ether yields yellow crystals with a melting point of 103°-105°C.

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Example 2

At 0°C, 3 g of ethylamine gas are passed into a solution of 3.7 g of 2,4,6-trichloro-5-nitro-pyrimidine and 50 ml of ethanol. The solution is then kept for 30 minutes at 5° to 10°C and subsequently evaporated to dryness in vacuo at 30°C. The residue is washed with water and dried. The 2-chloro-4,6-bis-ethylamino-5-nitro-pyrimidine has a melting point of 130°-132°C. 2-methoxy-4,6-bis-ethylamino-5-nitro-pyrimidine according to Example 1b is obtained by heating a solution of 2-chloro-4,6-bis-ethylamino-5-nitropyrimidine in methanol in the presence of sodium methylate.

Example 3

30 g (0.1 mol) of 2-methyl-mercapto-4-ethylamino-5-nitro-6-(3-pentyl-amino)-pyrimidine are dissolved in 400 ml of methanol. A solution of 8.1 g (0.15 mol) of sodium methylate in 100 ml of methanol is added together with 20 ml of triethylamine to the previously prepared solution. The mixture is refluxed for 16 hours, evaporated, and the residue is treated with 200 ml of water. After extracting 3 times with ether, the extracts are dried over MgSO₄, dried, filtered, and the ethereal solution is evaporated, to leave as residue 21.1 g of 2-methoxy-4-ethylamino-5-nitro-6-(3-pentylamino)-pyrimidine with a boiling point of 162°C/0.001 Torr (74.5 % of theory).

		C	H	N	S
Analysis:	calc.	50,87	7,47	24,72	-
	found	51,53	7,66	24,45	< 0.3

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Example 4

20.7 g of 2-methyl-4,6-dichloro-5-nitro-pyrimidine are dissolved in 300 ml of alcohol and then 12 ml of triethylamine are added. Subsequently 6 g of ethylamine are passed in or added dropwise at 25°-30°C in an ice bath. The reaction mixture is stirred for 1/2 hour at room temperature, then evaporated, and the residue is treated with 300 ml of water. The precipitate is filtered off with suction and the filter residue is washed with water until the runnings contain no more chlorine ions. The product is then dried in a water jet vacuum at 50°C, to yield 2-methyl-4,6-bis-ethyl-amino-5-nitro-pyrimidine with a melting point of 109°-110°C.

Example 5

a) 30 ml of triethylamine are added to 32.5 g (0.156 mol) of 2-methyl-4,6-dichloro-5-nitro-pyrimidine. At -18°C, 3.5 g of isopropylamine (0.16 mol) are added dropwise and the mixture is then stirred for 1 1/4 hours at this temperature. The mixture is subsequently poured on 4 litres of water, the precipitate is filtered off with suction, and washed 3 times with water. The crude product is dried at 50°C and 11 Torr for 16 hours, to yield 26.4 g of 2-methyl-4-chloro-5-nitro-isopropylamino-pyrimidine with a melting point of 69°-72°C. The pure substance (recrystallised from hexane) melts at 77°-79°C.

b) 10 ml of triethylamine are added to 8.05 g (0.035 mol) of 2-methyl-4-chloro-5-nitro-6-isopropylamino-pyrimidine. While

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cooling with ice, 7.3 g (0.1 mol) of sec- butylamine are slowly added dropwise and the mixture is stirred for 16 hours at room temperature. The reaction solution is evaporated, the residue suspended in 500 ml of water and extracted 3 times with ether, to yield 9.0 g of 2-methyl-4-isopropylamino-6-sec.-butylamino-5-nitro-pyrimidine (36.5 %) as an oil.

Example 6

5 ml of triethylamine are added to a solution of 5.4 g (0.025 mol) of 2-methyl-4-ethylamino-5-nitro-6-chloro-pyrimidine (m.p. 58°-61°C and manufactured in a manner analogous to that of Example 5a) in 150 ml of absolute alcohol and then 2.6 g (0.03 mol) of 3-aminopentane are added. The mixture is evaporated after 2 hours, the residue is treated with about 300 ml of water, and extracted twice with ether. The combined ethereal extracts are dried with MgSO_4 , filtered and evaporated, to yield 7.5 g of 2-methyl-4-ethylamino-5-nitro-6-(3'-pentyl-amino)-pyrimidine with a boiling point of 140°C/0.001 Torr.

Analysis:	calc.	C	H	N	Cl
		53,91	7,92	26,20	-
	found	53,86	7,95	25,83	<0,1

Example 7

19.4 g (0.1 mol) of 4,6-dichloro-5-nitro-pyrimidine are dissolved in 250 ml of alcohol and subsequently 22.5 g

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of ethylamine (0.5 mol) are passed into this solution at a maximum temperature of 40°C (ice bath). The mixture is stirred for 15 minutes, then evaporated, and the residue is treated with water. The suspension is filtered with suction and washed 3 times with water. After drying for 16 hours at 50°C and 11 Torr there are obtained 19.9 g of 4,6-bis(ethylamino)-5-nitro-pyrimidine (m.p. 80°-81°C); m.p. 81°-82°C after recrystallisation from hexane.

		C	H	N	Cl
Analysis:	calc.	45,09	6,20	33,15	+
	found	45,57	6,11	33,03	< 0,1

Example 8

5.4 g of 4-isopropylamino-5-nitro-6-chloro-pyrimidine (J.Chem.Soc. 1970/494) (0.025 mol) are dissolved in alcohol and the solution is treated with 5 ml of triethylamine. 3.5 g (0.04 mol) of pentyl-(3)-amine are added at room temperature and the mixture is subsequently refluxed for 16 hours at about 100°C bath temperature. The mixture is evaporated, the residue treated with about 200 ml of water and extracted 3 times with ether. These ethereal extracts are dried over MgSO₄ and evaporated. The residue contains the desired 4-isopropylamino-5-nitro-6-(3-pentylamino)-pyrimidine.

Example 9

15.6 g of 2-methylmercapto-4-isopropylamino-5-nitro-6-(3-pentyl-amino)-pyrimidine (0.05 mol) are dissolved in

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250 ml of alcohol. Then 20 ml of triethylamine and 3 g of dimethylamine are added. The reaction mixture is kept for 16 hours under high pressure (12 bar) at 100°C, until no more starting material can be detected in a thin-layer chromatogram (silica gel, hexane/acetone 5:1). The mixture is evaporated, the residue is treated with water and extracted twice with ether. The ethereal extracts are dried over MgSO_4 , filtered and evaporated, to yield 13.5 g of 2-dimethylamino-4-isopropylamino-5-nitro-6-(3-pentylamino)-pyrimidine; b.p. 160°C/0.001 Torr

		C	H	N	S
Analysis:	calc.	54,17	8,44	27,08	-
	found	55,06	8,54	26,55	< 0,5

Example 10

1.15 g (0.005 mol) of 2,4,6-trichloro-5-nitropyrimidine are dissolved in 50 ml of alcohol and the solution is then treated with 2.9 g (0.05 mol) of isopropylamine. The mixture is stirred for 3 hours at room temperature after the temperature has first risen to 35°C, and then it is evaporated. The residue is treated with 100 ml of water and extracted twice with ether. The ethereal extract is dried over MgSO_4 for 4 hours, filtered, and evaporated, to yield 1.1 g of 2,4,6-tri-isopropylamino-5-nitro-pyrimidine as an oil; b.p. 185°C at 0.001 Torr.

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Example 11

a) 10 mols of isobutyronitrile and 10 mols of abs. ethanol are mixed and 10 mols of HCl gas are passed in at a maximum temperature of 30°C. After the mixture has been stirred overnight, a solution of 10 mols of ammonia in 1.5 litres of abs. ethanol is added dropwise and the batch is stirred overnight. The reaction solution is filtered and concentrated to dryness. The residue is dissolved in about 2 litres of methanol and this solution is added to a solution of 30 mol of NaOCH₃ in 3.5 litres of methanol. After the addition, the mixture is stirred overnight. The reaction mixture is subsequently concentrated, the residue taken up in water and acidified with HCl, whereupon 4,6-dihydroxy-2-isopropyl-pyrimidine crystallises out; m.p. 290°C-300°C.

b) 220 g of 4,6-dihydroxy-2-isopropyl-pyrimidine are added at 0°C to 500 ml of 100 % nitric acid and the mixture is stirred for 1 hour. Subsequently the nitration mixture is poured on ice water, filtered, washed with water, and dried in vacuo over P₂O₅, to yield 110 g of 4,6-dihydroxy-2-isopropyl-5-nitro-pyrimidine; m.p. 300°C.

c) 110 g (0.55 mol) of 4,6-dihydroxy-2-isopropyl-5-nitro-pyrimidine are added to 400 ml of POCl₃. Then 110 ml of N,N-diethyl amiline are added dropwise, whereupon the temperature rises to 45°C. The mixture is refluxed for 1 hour and, after cooling, poured on ice water, which is subsequently filtered. The residue is extracted with ether to yield 65 g

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4,6-dichloro-2-isopropyl-5-nitro-pyrimidine; m.p. 32°C.

d) 5 g of 4,6-dichloro-2-isopropyl-3-nitro-pyrimidine are dissolved in 100 ml of abs. ethanol, the solution is treated with 5 ml of triethylamine and 5.9 g of isopropylamine and stirred overnight. The reaction mixture is evaporated, the product then taken up in water, and extracted with ether, to yield 5.5 g of 2-isopropyl-4,6-bis(diisopropylamino)-5-nitro-pyrimidine; m.p. 45°C.

Example 12

a) 4.72 g (0.02 mol) of 4,6-dichloro-2-isopropyl-5-nitro-pyrimidine are dissolved in 100 ml of abs. ethanol. At -30°C, 2 g (0.02 mol) of triethylamine and 0.9 g (0.02 mol) of ethylamine are added and the mixture is then stirred for 4 hours at -20°C and for 6 hours at 0°C. Subsequently the reaction mixture is concentrated to dryness and the product is taken up in water and extracted with ether, to yield 4.5 g of 2-isopropyl-4-ethylamino-5-nitro-6-chloro-pyrimidine; m.p. 50°C.

b) 0.02 mol of 4-ethylamino-6-chloro-2-isopropyl-5-nitro-pyrimidine is dissolved in 100 ml of abs. ethanol. The solution is treated with 0.05 mol of triethylamine and 0.05 mol of isopropylamine and the mixture is stirred overnight. The

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reaction mixture is then concentrated to dryness and the product is taken up in water and extracted with ether. The yield of 2-isopropyl-4-ethylamino-5-isopropylamino-5-nitro-pyrimidine is 90 %; $n_D^{20} = 1.5660$.

Example 13

5.25 g (0.02 mol) of 4,6-dichloro-5-nitro-2-trifluoromethyl-pyrimidine (J.Org.Chem. 26 (1961), pp. 4504-8) are dissolved in 150 ml of abs. ethanol. The solution is treated with 5 ml of triethylamine (0.05 mol) and 4.5 g (0.1 mol) of ethylamine and the mixture is stirred overnight, then evaporated to dryness. The residue is taken up in ether and washed with water. The ethereal phase is dried and concentrated to yield 5.5 g of 4,6-bis-ethylamino-5-nitro-2-trifluoromethyl-pyrimidine; m.p. 60° - 65° C.

Example 14

a) 5.25 g (0.02 mol) of 4,6-dichloro-5-nitro-2-trifluoromethyl-pyrimidine are dissolved in 100 ml of abs. ethanol and the solution is cooled to -30° C. At this temperature, 2.0 g (0.02 mol) of triethylamine and 0.9 g (0.2 mol) of ethylamine are added. The mixture is stirred first for 4 hours at -20° C to -30° C and then for 6 hours at 0° C. After it has been left to stand overnight at 20° C, the reaction mixture is concentrated to dryness. The residue is taken up in ether and the solution washed with water. The ethereal phase is dried and concentrated to yield 5.3 g of 4-ethylamino-6-chloro-5-nitro-2-trifluoromethyl-pyrimidine as a pale yellow oil; $n_D^{20} = 1.4985$.

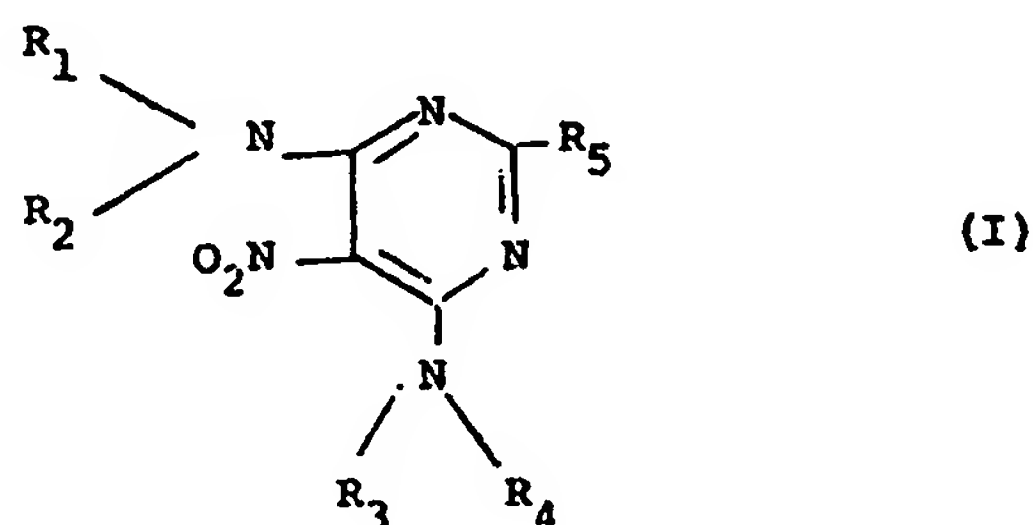
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b) 5.4 g (0.02 mol) of 4-ethylamino-6-chloro-5-nitro-2-trifluoromethyl-pyrimidine are dissolved in 100 ml of abs. ethanol. The solution is treated with 2.3 g of triethylamine (0.023 mol) and 1.7 g (0.023 mol) of 2-amino-butane and the mixture is stirred overnight. After the mixture has been evaporated, the product is taken up in water and extracted with ether to yield 4.5 g of 4-ethylamino-5-nitro-6-(2-butylamino)-2-trifluoromethyl-pyrimidine; $n_D^{20} = 1.5209$.

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. An agent for inhibiting plant growth, in particular a herbicidal agent, which contains as active substance at least one 5-nitropyrimidine derivative of the formula I



wherein R_1 represents an alkyl radical with 1 to 6 carbon atoms, an alkenyl radical with at most 5 carbon atoms, a C_3 - C_6 cycloalkyl (unsubstituted or carrying a methyl or ethyl substituent), alkoxyalkyl, cyanoalkyl, or hydroxyalkyl radical, R_2 and R_3 each independently represents hydrogen or an alkyl radical with 1 to 4 carbon atoms, R_4 represents a lower alkyl C_3 - C_4 alkenyl or C_3 - C_6 cycloalkyl (unsubstituted or carrying a methyl or ethyl substituent) radical, and R_5 represents hydrogen or a lower alkyl, haloalkyl, alkoxy, alkylamino, or dialkylamino radical or represents a halogen atom, or which contains an addition salt of such a nitropyrimidine derivative with inorganic or organic acids, in admixture with a solid or liquified gaseous diluent or in admixture with a liquid diluent other than a solvent of a molecular weight less than 200 except in the

presence of a surface active agent.

2. An agent according to claim 1, which contains a 5-nitropyrimidine derivative of the formula I, or an addition salt thereof, wherein the substituted amino radicals in 4- and 6-position are different from each other.
3. An agent according to claim 1 or 2, wherein at least one of the radicals R_1 and R_4 in the nitropyrimidine derivative of the formula I is a branched alkyl radical with 3 to 5 carbon atoms.
4. An agent according to any one of claims 1 to 3, wherein the radical R_5 in the nitropyrimidine derivative of the formula I represents one of the radicals CH_3 , C_2H_5 , OCH_3 , CF_3 , or CCl_3 .
5. An agent according to any one of claims 1 to 4, wherein the active ingredient is 2-methyl-4-ethylamino-4-(3'-pentylamino)-5-nitro-pyrimidine.
6. A method for eradicating weeds from crop growing areas containing a growing crop which comprises applying to the crop areas a nitropyrimidine of the formula I according to claim 1, or an addition salt thereof with acids, or an agent which contains a nitropyrimidine of the formula I according to Claim 1 or an addition salt thereof with acids.
7. A method of claim 6 for the post-emergent control of *Avena fatua* in grain crops which comprises applying to the crop areas as the active ingredient the compound 2-methyl-4-

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ethylamino-5-nitro-6-(3'-pentylamino)-pyrimidine.

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